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(54) Novel phenylureas.

(57) Novel substituted N-(heterocyclic-substituted phenyl)-
N'-benzoylureas, processes for producing these com-
pounds, compositions thereof and the use of the compounds
for the control of pests.

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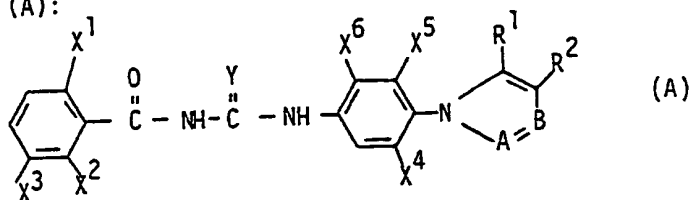
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Case 133-0637

NOVEL PHENYLUREAS

The present invention relates to novel substituted N-(heterocyclic-substituted phenyl)-N'-benzoylureas, to processes for producing these compounds, to intermediates therefor, to compositions thereof and to the use of the compounds for the control of pests, and in particular for the control of insects and acarids.

More particularly, the compounds of the present invention are represented by the following formula (A):



- 10 wherein, each of X^1 , X^2 , X^3 and X^5 is independently hydrogen, halogen or C_{1-4} alkyl;
 X^4 is hydrogen, halogen, unsubstituted or halogenated C_{1-4} alkyl or COOR;
 X^6 is hydrogen, halogen, C_{1-8} alkyl or COOR';
 Y is oxygen or sulfur;
 15 A is nitrogen or $C-R^4$;
 B is nitrogen or $C-R^3$;
 each of R^1 and R^4 is independently hydrogen, halogen, halogenated C_{1-8} alkyl, unsubstituted or halogenated C_{1-8} alkoxy, unsubstituted or halogenated C_{1-8} alkylthio or; aryl, aryloxy or arylthio unsubstituted or
 20 substituted with 1 to 4 halogen atoms or with a CF_3 ,
 C_{1-4} alkyl or C_{1-4} alkoxy group and 0 to 3 halogen atoms;
 each of R^2 and R^3 is independently hydrogen; halogen; cyano; unsubstituted or halogenated C_{1-8} alkyl; unsubstituted or halogenated C_{1-8} alkoxy; unsubstituted or halogenated C_{1-8} alkylthio; COOR"; aryl,
 25 aryloxy or arylthio unsubstituted or substituted with 1 to 4 halogenatoms
 or with a C_{1-4} alkyl, C_{1-4} alkoxy or CF_3 group and 0 to 3 halogen atoms;
 or either R^1 and R^2 or R^2 or R^3 can together form a bridging group of
 4 carbon atoms, saturated or unsaturated, and optionally substituted
 with 1 to 4 halogen atoms or with a trifluoromethyl group and 0 to 3
 30 halogen atoms;
 each of R , R' and R'' is hydrogen or C_{1-8} alkyl;
 with the proviso that where A is $C-R^4$ and B is $C-R^3$, not all of R^1 ,
 R^2 , R^3 and R^4 may be hydrogen.

In the practice of the present invention, Y is preferably oxygen.

A is preferably nitrogen.

Where A is nitrogen, B is preferably C-R³.

5 Where any of the substituents X¹-X⁶ and R¹-R⁴ is or comprises halogen, such halogen is conveniently selected from bromo, chloro and fluoro.

Where any of X¹-X⁶ is C₁₋₈alkyl, it is preferably of one to four carbons and is more preferably of one or two carbons.

Where any of R, R' and R'' is C₁₋₈alkyl, it is preferably of one to four 10 carbons and is more preferably of one or two carbons.

The terms halogenated C₁₋₈alkyl, halogenated C₁₋₈alkoxy and halogenated C₁₋₈alkylthio refer to C₁₋₈alkyl, C₁₋₈alkoxy and C₁₋₈alkylthio, respectively, substituted by one to six, preferably one to three halogens; such halogen is preferably chloro or fluoro.

15 An example of a preferred halogenated C₁₋₈alkyl group is CF₃.

The term aryl as used herein (as such or in the terms aryloxy or arylthio) refers to an aromatic ring system such as naphthyl, phenyl, pyridyl and thienyl; preferably phenyl. Where such aryl is substituted it may bear from 1 to 4, preferably 1 or 2 substituents. Thus aryl, aryloxy and arylthio is preferably 20 unsubstituted or substituted with one methyl, methoxy or CF₃ group and zero or one halogen atoms or with one or two halogen. Particularly preferred substituted aryl significances are halophenyl, dihalophenyl, methylphenyl and trifluoro-methylphenyl.

Preferably not more than one of R¹, R², R³ and R⁴ is unsubstituted or 25 substituted aryl, aryloxy or arylthio.

X¹ is preferably H or halogen, more preferably chloro or fluoro.

X² is preferably hydrogen or halogen; such halogen is preferably fluoro.

X³ is preferably hydrogen or halogen, more preferably hydrogen.

X⁴ conveniently signifies hydrogen, halogen, C₁₋₄alkyl, CF₃ or COOR; it 30 is preferably hydrogen, chloro, bromo, methyl or CF₃.

X⁵ is preferably hydrogen, C₁₋₄alkyl or halogen; it is more preferably hydrogen, chloro or methyl.

X⁶ is preferably hydrogen or halogen, more preferably H or F.

R¹ conveniently signifies hydrogen, halogen, CF₃, unsubstituted or unsub- 35 stituted aryl, C₁₋₄alkoxy or together with R² forms a bridging group of 4

carbon atoms. R^1 is preferably hydrogen, bromo, chloro, CF_3 , or unsubstituted or substituted phenyl, more preferably hydrogen or chloro.

R^2 conveniently signifies hydrogen, halogen, CF_3 , C_{1-4} alkyl, $COOR'$, cyano, unsubstituted or substituted phenyl, or together with either R^1 or R^3 forms a bridging group of 4 carbon atoms. R^2 is preferably hydrogen, halogen, CF_3 or unsubstituted or substituted phenyl. R^2 is more preferably hydrogen, halogen, CF_3 or un-, mono- or disubstituted phenyl, and is particularly H, Cl or Br.

R^3 conveniently signifies hydrogen, halogen, CF_3 , C_{1-4} alkyl, unsubstituted or substituted phenyl or together with R^2 forms a bridging group of 4 carbon atoms. R^3 is preferably hydrogen, halogen, CF_3 , C_{1-4} alkyl or un-, mono- or disubstituted phenyl, particularly H, Cl, Br, CF_3 , 4-chlorophenyl or 4-bromophenyl.

Where R^1 and R^2 together form a bridging group this is preferably of the formula $CH=CH-CH=CH$; such group is preferably unsubstituted or substituted by 1 or 2 halogen atoms; such halogen is preferably chloro.

Where R^2 and R^3 together form a bridging group this is preferably of the formula $(CH_2)_4$. Such group is preferably unsubstituted or substituted by 1 or 2 halogen atoms; more preferably it is unsubstituted.

Accordingly, in a preferred subgroup of compounds of formula (A) each of X^1 , X^2 and X^3 is independently H or halogen,

X^4 is H, halogen, CH_3 or CF_3 ,

X^5 is H, halogen or CH_3 , X^6 is H or halogen, Y is O, A is N, B is $C-R^3$, each of R^1 and R^2 is independently H, halogen or CF_3 .

R^3 is H, halogen, C_{1-4} alkyl or CF_3 whereby one of R^1 , R^2 and R^3 may also be halophenyl, dihalophenyl, methylphenyl or trifluoromethylphenyl and/or

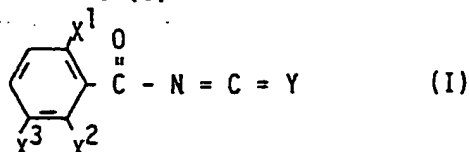
R^1 and R^2 together may form a bridging group of the formula $CH=C-CH=CH$, which group is unsubstituted or mono- or dihalogenated, or

R^2 and R^3 together form a bridging group of formula $(CH_2)_4$.

The compounds of formula (A) can have one or more asymmetric centers, geometric or positional isomers. The present invention includes each of such isomers or mixtures thereof. In the examples hereinafter such isomers are obtained as mixtures unless otherwise specified.

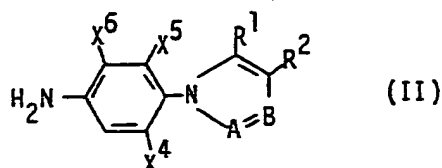
The compounds of formula (A) are obtained by

a) reacting a compound of formula (I)



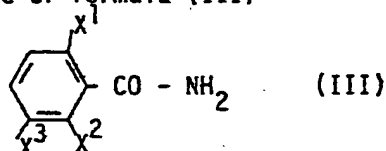
wherein X^1 , X^2 , X^3 and Y are as defined above,

with a compound of formula (II)



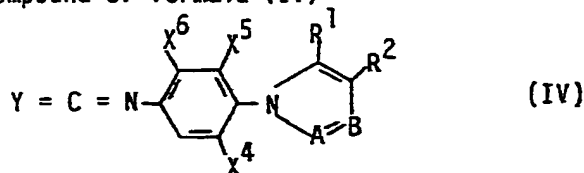
5 wherein X^4 , X^5 , X^6 , R^1 , R^2 , A and B are as defined above,

or b) by reacting a benzamide of formula (III)



wherein X^1 , X^2 and X^3 are as defined above,

with a compound of formula (IV)



wherein Y, R^1 , R^2 , X^4 , X^5 , X^6 , A and B are as defined above.

10 The reaction of compounds of formula I with compounds of formula II (process a) may be effected under the conditions known for the preparation of N-benzoyl-N'-phenylureas from the corresponding isocyanates and anilines.

The reaction is conveniently carried out in a solvent which is inert under the reaction conditions, e.g. methylene chloride or dimethylformamide. A suitable reaction temperature may vary from -10°C to the boiling point of the solvent used, and preferably is about room temperature or moderately above or below room temperature, e.g. between 15 and 25°C .

The reaction of compounds of formula III with compounds of formula IV (process b) may be effected under the conditions known for the preparation of N-benzoyl-N'-phenylureas from the corresponding benzamides and phenylisocyanates. The reaction is conveniently carried out in a solvent which is inert

under the reaction conditions. A suitable reaction temperature is from 0° to 120°C, preferably at the boiling point of the solvent used. The reaction is optionally effected in the presence of an organic base, such as pyridine.

- 5 The compounds of formula (A) may be recovered from the reaction mixture in which they are formed by working up by established procedures.

The compounds of formula I can be synthesized by treating the corresponding benzamide with oxalyl chloride or by reacting the corresponding benzoyl chloride with ammonium thiocyanate.

- 10 The aniline derivatives of formula II can be prepared by reduction of catalytic hydrogenation of the corresponding nitro compounds.

The isocyanates and isothiocyanates of formula IV can be produced by reaction of the derivatives of formula II with phosgene or thiophosgene.

- The starting materials and reagents employed in the processes described
15 herein are either known or, insofar as they are not known, may be produced in a manner analogous to the process described herein or to known processes.

The compounds of formula (A) are chitin inhibitors as indicated by tests with i.a. third instar larvae of *Manduca sexta*, *Musca domestica*, *Heliothis virescens* and *Spodoptera exigua*, fourth instar larvae of *Aedes aegypti*, first
20 instar larvae of *Dermestes maculatus*. They are accordingly indicated for use as pest controlling agents, particularly for the control of insects, mites and ticks.

In view of their interesting activity, particularly with regard to the level and spectrum of activity, the compounds of formula (A) offer an advantageous alternative for known chitin inhibitors, such as those disclosed in US
25 Pat. Spec. 3 748 356 and UK Pat. Spec. 2 134 518A.

The compounds of formula (A) can be effective control agents for insects of, for example, the orders Lepidoptera, Hemiptera, Homoptera, Coleoptera, Diptera, Orthoptera and Siphonaptera, and other insects, as well as for mites
30 and ticks of the class Acari, including mites of the families Tetranychidae and Tarsonemidae and ticks of the families Argasidae and Ixodidae. The compounds can be applied to the pest or its locus in a pest-controlling amount, usually of the order of 0.001 microgram to 100 microgram per insect, mite or tick, depending on the mode and conditions of application as well as
35 on the pest involved.

Additionally, compounds of formula (A) may possess a repellent and/or anti-feedant action on terrestrial snails and slugs.

In the use of the compounds of formula (A) for combatting pests, a compound of formula (A), or mixtures thereof, can conveniently be employed as pesticidal compositions in association with acceptable diluent(s) for application to the pest or its locus. Such compositions also form part of the present invention.

Suitable formulations contain from 0.01 to 99% by weight of active ingredient, from 0 to 20% of surfactant from 1 to 99.99% of diluent(s). Higher ratios of surfactant to active ingredient are sometimes desirable and are achieved by incorporation into the formulation or by tank mixing. Application forms of a composition generally contain between 0.01 and 25% by weight of active ingredient. Lower or higher levels of active ingredient can, of course, be present depending on the intended use, the physical properties of the compound and the mode of application. Concentrate forms of a composition intended to be diluted before use generally contain between 2 and 90%, preferably between 5 and 85% by weight of active ingredient.

Useful formulations of the compounds of formula (A) include dusts, granules, suspension concentrates, wettable powders, flowables and the like. They are obtained by conventional manner, e.g. by mixing a compound of formula (A) with the diluent(s) and optionally with other ingredients.

Alternatively, the compounds of formula (A) may be used in micro-encapsulated form.

The compounds of formula (A) can be combined with a cyclodextrin to make a cyclodextrin inclusion complex for application to the pest or its locus.

Agriculturally acceptable additives may be employed in the pesticidal compositions to improve the performance of the active ingredient and to reduce foaming, caking and corrosion, for example.

"Surfactant" as used herein means an agriculturally acceptable material which imparts emulsifiability, spreading, wetting, dispersibility or other surface-modifying properties. Examples of surfactants are sodium lignin-sulphonate and lauryl sulfate.

"Diluent" as used herein means a liquid or solid agriculturally acceptable material used to dilute a concentrated material to a usable or desirable strength. For dusts or granules it can be e.g. talc, kaolin or diatomaceous earth, for liquid concentrate forms for example a hydrocarbon such as xylene or an alcohol such as isopropanol, and for liquid application forms i.a. water or diesel oil.

The compositions of this invention can also comprise other compounds having biological activity, e.g. compounds having similar or complementary pesticidal or insect growth regulating activity or compounds having antidotal, fungicidal, herbicidal or insect attractant activity.

The following examples are provided to illustrate the practice of the present invention. Temperature is given in degrees Centigrade. RT means room temperature. Parts and percentages are by weight. The symbols *, = and + when used in connection with melting points means "gas", "softens" and "decomposes" respectively. DMF means dimethyl formamide.

COMPOSITION EXAMPLES

Example A: Dust

	Compound 14	5.1%
20	kaolin	94.9%

Example B: Flowable

	Compound 14	48.0%
	dispersant	4.0%
	thickener	0.6%
25	antifoam	0.1%
	water	41.3%
	propylene glycol	6.0%

Example C: Wettable Powder

30	Compound 17	81.0%
	kaolin	14.8%
	dispersant	4.0%
	wetting agent	0.2%

The ingredients are mixed and milled until the mean particle size is about 5 micron.

PREPARATION OF FINAL UREASExample 1: N-4-(4-chloro-1-pyrazolyl)phenyl-N'-2,6-difluorobenzoylurea

2,6-Difluorobenzoyl isocyanate (0.47 g, 2.6 mmol) is added dropwise to a solution of 4-(4-chloro-1-pyrazolyl)aniline (0.50 g, 2.6 mmol) in 8 ml of methylene chloride. The mixture is stirred for 30 min., then diluted with methylene chloride and filtered. The solid is washed with ether and dried to give N-4-(4-chloro-1-pyrazolyl)phenyl-N'-2,6-difluorobenzoylurea (compound 1 under Table A).

10 Example 2: N-3,5-dichloro-4-(1-pyrazolyl)phenyl-N'-2,6-difluorobenzoylurea

To a solution of 3,5-dichloro-4-(1-pyrazolyl)aniline (0.17 g, 0.75 mmol) in 7 ml of methylene chloride and 1 ml of DMF is added 2,6-difluorobenzoyl isocyanate (0.14 g, 0.75 mmol). The resulting mixture is stirred for 5 min., then diluted with ethyl acetate, washed with water and with brine, and dried. After the solvent is evaporated off, ether is added to the solid residue, the suspension is filtered and the solid is washed with ether and dried to give N-3,5-dichloro-4-(1-pyrazolyl)phenyl-N'-2,6-difluorobenzoylurea (compound 2 under Table A).

Example 3

20 Following generally the procedures of Example 1 or 2, each of the final product ureas under Tables A and B and those listed under column I below is prepared from the corresponding aniline and benzoyl isocyanate or benzoyl isothiocyanate intermediates.

TABLE A

Compounds of formula (A) wherein Y is O, A is N and B is CR₃ :





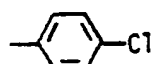
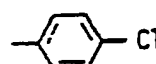




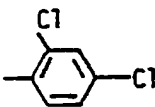
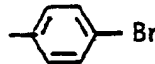


	Cpd	X ¹	X ²	X ³	X ⁴	X ⁵	X ⁶	R ¹	R ²	R ³	m.p. (°C)
10	1	F	F	H	H	H	H	H	Cl	H	240-242
	2	F	F	H	Cl	Cl	H	H	H	H	211-212
	3	F	F	H	Cl	Cl	H	H	Cl	H	229-230
	4	F	F	H	Cl	Cl	H	H	Br	H	233-235
	5	F	F	H	Cl	Cl	H	H	CF ₃	CF ₃	220-223
15	6	F	F	H	Cl	Cl	H	H	H	Cl	217-219
	7	F	F	H	Cl	Cl	H	H	Br	Br	224-227
20	8	F	F	H	Cl	Cl	H	H	H		210-212
	9	F	F	H	Cl	Cl	H	H		H	246-247
	10	F	F	H	Cl	Cl	H	H	H	CF ₃	202.5- 203.5
	11	F	F	H	Cl	Cl	H	H	CF ₃	H	222-223
	12	F	F	H	Cl	Cl	H	Cl	H	CF ₃	206-207
25	13	F	F	H	Cl	Cl	H	H	H	C(CH ₃) ₃	204-205
	14	F	F	H	Cl	Cl	H	H	Cl		206.5- 208.5
	15	F	F	H	Cl	Cl	H	H	Cl	Cl	231-233
30	16	F	F	H	Cl	Cl	H	H	Cl	CF ₃	222.5-224
	17	F	F	H	Cl	Cl	H	Cl	Cl	CF ₃	203-204
	18	F	F	H	Cl	Cl	H	CF ₃	H	CF ₃	212.5-214
	19	F	F	H	H	H	H	CF ₃	H	CF ₃	211.5-212
	20	F	F	H	H	H	H	Cl	H	CF ₃	197-199
	21	F	F	H	H	Cl	H	H	Cl	H	230-231

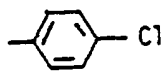
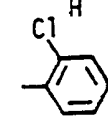
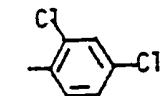
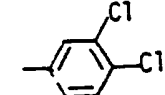

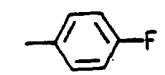
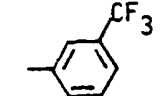

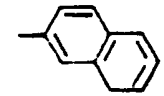
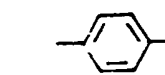
TABLE A (cont.)

<u>Cpd</u>	<u>X¹</u>	<u>X²</u>	<u>X³</u>	<u>X⁴</u>	<u>X⁵</u>	<u>X⁶</u>	<u>R¹</u>	<u>R²</u>	<u>R³</u>	<u>m.p.</u> <u>(°C)</u>
535	F	F	H	Cl	H	H	H	Cl		
36	F	F	H	CF ₃	H	H	H	Cl		242-244
37	F	F	H	CF ₃	H	H	Cl	H	CF ₃	192.5-195
¹⁰ 38	F	F	H	Cl	Cl	H	Cl	Cl	Cl	236-238
39	F	F	H	Cl	Cl	H	H	Br		204-206
40	F	F	H	Cl	Cl	H	Br	Br	Br	249-250
¹⁵ 41	F	F	H	Cl	Cl	H	CF ₃	H	Cl	209-211
42	F	F	H	H	H	F	H	Cl		121.5-122.5
43	F	F	H	Cl	H	F	H	Cl		238-240
²⁰ 44	F	F	H	CH ₃	H	H	H	Cl		236-238
45	F	F	H	Cl	H	CH ₃	H	Cl		208-210
²⁵ 46	F	F	H	Cl	Cl	H	H		H	232-234
47	F	F	H	Cl	Cl	H	H		H	253-254
³⁰ 48	F	F	H	CH ₃	CH ₃	H	H	Cl		217-219
49	F	F	H	Cl	Cl	H	OCH ₃	Cl		216-217
³⁵ 50	F	F	H	Cl	Cl	H	H	C(O)OCH ₂ CH ₃	H	213-215

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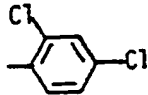
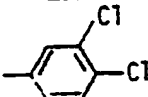
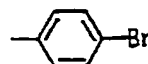

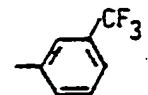

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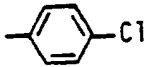
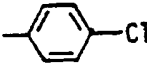

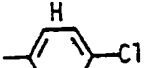

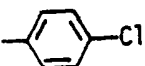
Cpd	X ¹	X ²	X ³	X ⁴	X ⁵	X ⁶	R ¹	R ²	R ³	m.p. (°C)
5 51	F	F	H	C(O)OCH ₃	H	H	H	Cl		210-212
52	F	F	H	Cl	H	H	Cl	H	CF ₃	207.5- 208.5
53	F	F	H	Cl	H	H	H	Br	H	226-228
10 54	F	F	H	CF ₃	H	H	H	Br	H	206-208
55	F	F	H	Cl	Cl	H	H	H		230-232
56	F	F	H	Cl	Cl	H	H	H		231-232
15 57	F	F	H	Cl	Cl	H	H	H		224-225
58	F	F	H	Cl	Cl	H	H	H		224-225
20 59	F	F	H	Cl	Cl	H	H	H		222-224
60	F	F	H	Cl	Cl	H	H	H		199-200
25 61	F	F	H	Cl	Cl	H	H	H		226-228
62	F	F	H	Cl	Cl	H	H	H		228-229
30 63	F	F	H	Cl	Cl	H	H	CN	H	246-248
64	F	H	H	Cl	Cl	H	Cl	Cl	CF ₃	193- 194.5
35 65	F	H	H	Cl	Cl	H	H	Cl		198-200

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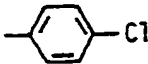
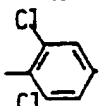
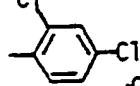
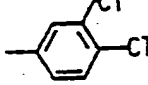
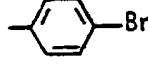

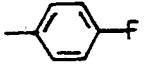
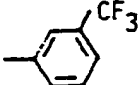

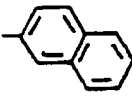
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TABLE A (cont.)

Cpd	X ¹	X ²	X ³	X ⁴	X ⁵	X ⁶	R ¹	R ²	R ²	m.p. (°C)
66	F	H	H	Cl	H	H	Cl	H	CF ₃	202-203
67	F	H	H	Cl	H	H	H	Br	H	213-215
⁵ 68	F	H	H	CF ₃	H	H	H	Br	H	170-172
69	F	H	H	Cl	Cl	H	H	H		215-216
¹⁰ 70	F	H	H	Cl	Cl	H	H	H		234-236
71	F	H	H	Cl	Cl	H	H	H		218-219
¹⁵ 72	F	H	H	Cl	Cl	H	H	H		199-201
73	F	H	H	Cl	Cl	H	H	H		202-204
74	CH ₃	H	H	Cl	Cl	H	Cl	Cl	CF ₃	211-212.5
²⁰ 75	CH ₃	H	H	Cl	Cl	H	H	Cl		243-245
76	Cl	H	F	Cl	Cl	H	Cl	Cl	CF ₃	211-212.5
77	Cl	F	H	Cl	Cl	H	Cl	Cl	CF ₃	220.5-222
²⁵ 78	Cl	Cl	H	Cl	Cl	H	Cl	Cl	CF ₃	231.5-232.5
79	Cl	H	H	H	H	H	H	Cl	H	
80	Cl	H	H	Cl	Cl	H	H	H	H	200-202
81	Cl	H	H	Cl	Cl	H	H	Cl	H	236-238
³⁰ 82	Cl	H	H	Cl	Cl	H	H	Br	H	234-236
83	Cl	H	H	Cl	Cl	H	H	CF ₃	CF ₃	195-196
84	Cl	H	H	Cl	Cl	H	H	H	Cl	202-203
³⁵ 85	Cl	H	H	Cl	Cl	H	H	Br	Br	208-210

Cpd	X ¹	X ²	X ³	X ⁴	X ⁵	X ⁶	R ¹	R ²	R ³	m.p. (°C)
86	Cl	H	H	Cl	Cl	H	H	H		201.5-203
5 87	Cl	H	H	Cl	Cl	H	H		H	227-230
88	Cl	H	H	Cl	Cl	H	H	H	CF ₃	
89	Cl	H	H	Cl	Cl	H	H	CF ₃	H	207-208
10 90	Cl	H	H	Cl	Cl	H	Cl	H	CF ₃	209-210
91	Cl	H	H	Cl	Cl	H	H	H	C(CH ₃) ₃	200-201
92	Cl	H	H	Cl	Cl	H	H	Cl		229-231.5
15 93	Cl	H	H	Cl	Cl	H	H	Cl	Cl	220-227
94	Cl	H	H	Cl	Cl	H	H	Cl	CF ₃	202-203
95	Cl	H	H	Cl	Cl	H	Cl	Cl	CF ₃	203.5-204.5
20 96	Cl	H	H	Cl	Cl	H	CF ₃	H	CF ₃	204-205
97	Cl	H	H	H	H	H	CF ₃	H	CF ₃	
98	Cl	H	H	H	H	H	Cl	H	CF ₃	
99	Cl	H	H	H	Cl	H	H	Cl		225-226.5
25 100	Cl	H	H	Cl	H	H	H	Cl		198-199
101	Cl	H	H	CF ₃	H	H	H	Cl	CF ₃	183-185
102	Cl	H	H	CF ₃	H	H	Cl	H		
30 103	Cl	H	H	Cl	Cl	H	H	Br		222-224
104	Cl	H	H	Cl	Cl	H	Br	Br	Br	232-233
105	Cl	H	H	Cl	Cl	H	CF ₃	H	Cl	208-209

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TABLE A (cont.)

									133-0637	
Gpd	X ¹	X ²	X ³	X ⁴	X ⁵	X ⁶	R ¹	R ²	R ³	m.p. (°C)
106	Cl	H	H	Cl	Cl	H	Cl	Cl	Cl	222-224
5 107	Cl	H	H	CH ₃	CH ₃	H	H	Cl		216-218
108	Cl	H	H	Cl	H	H	H	Br	H	243-245
109	Cl	H	H	CF ₃	H	H	H	Br	H	184-186
10 110	Cl	H	H	Cl	Cl	H	H	H		184-187
111	Cl	H	H	Cl	Cl	H	H	H		211-213
15 112	Cl	H	H	Cl	Cl	H	H	H		220-221
113	Cl	H	H	Cl	Cl	H	H	H		210-211
114	Cl	H	H	CH ₃	Cl	H	H	Cl		240-242
20 115	Cl	H	H	Cl	Cl	H	H	H		191-192
116	Cl	H	H	Cl	Cl	H	H	H		150-151
25 117	Cl	H	H	Cl	Cl	H	H	H		220-222
118	Cl	H	H	Cl	Cl	H	H	H		228-229
30 119	Cl	H	H	H	Cl	H	Cl	H	CF ₃	209-210

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TABLE A (cont.)

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	<u>Cpd</u>	<u>x¹</u>	<u>x²</u>	<u>x³</u>	<u>x⁴</u>	<u>x⁵</u>	<u>x⁶</u>	<u>R¹</u>	<u>R²</u>	<u>R³</u>	<u>m.p.</u> <u>(°C)</u>
	149	Cl	H	H	Cl	Cl	H	4-Br-phenyl	H	H	218-220
5	150	Cl	H	H	Cl	Cl	H	" "	Cl	H	225-229
	151	F	F	H	Cl	Cl	H	" "	H	H	237-238
	152	F	F	H	Cl	Cl	H	" "	Cl	H	301-305
	153	F	F	H	Cl	Cl	H	H	H	4-CH ₃ - C ₆ H ₄	198-202
10	154	Cl	H	H	Cl	Cl	H	H	H	4-CH ₃ - C ₆ H ₄	205-210
	155	H	H	H	Cl	Cl	H	H	H	4-Br- C ₆ H ₄	256-259

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TABLE B

Compounds of formula (A) wherein X^3 and X^6 are H, Y is O and $R^1 + R^2$ is $CH=CH^1-CW^2=CH^3$ (with W^3 in ortho-position of B)

Cpd	X^1	X^2	X^4	X^5	A	B	W^1	W^2	W^3	m.p. (°C)
23	F	F	Cl	Cl	N	CH	H	H	H	
1024	F	F	Cl	Cl	N	C-Cl	H	H	H	235-237
25	F	F	Cl	Cl	N	C-Cl	H	H	Cl	
26	F	F	Cl	Cl	CH	N	Cl	Cl	H	225-228
27	F	F	Cl	H	CH	N	Cl	Cl	H	
1528	F	F	Cl	Cl	N	N	H	Cl	H	(*)
29	F	F	Cl	Cl	N	N	Cl	Cl	H	242-244
120	Cl	H	Cl	Cl	N	CH	H	H	H	
121	Cl	H	Cl	Cl	N	C-Cl	H	H	H	
20122	Cl	H	Cl	Cl	N	C-Cl	H	H	Cl	
123	Cl	H	Cl	Cl	CH	N	Cl	Cl	H	246-249
124	Cl	H	Cl	H	CH	N	Cl	Cl	H	225-228
25125	Cl	H	Cl	Cl	N	N	H	Cl	H	103-106
126	Cl	H	Cl	Cl	N	N	Cl	Cl	H	222-225
127	F	F	H	Cl	C-CF ₃	N	Cl	Cl	H	218-223

(*) isomer A : m.p. 196-198°
isomer B : m.p. 177-181°

30

128. N-3,5-dichloro-4-(2-indazolyl)phenyl-N'-2,6-difluorobenzoyl urea,
m.p. 209-210°;
129. N-3,5-dichloro-4-(2-indazolyl)phenyl-N'-2-chlorobenzoyl urea,
5 m.p. 216-217°;
130. N-3,5-dichloro-4-(4,5,6,7-tetrahydroisoindol-2-yl)phenyl-N'-2,6-difluoro-
benzoylurea, m.p. 240-242°;
131. N-3,5-dichloro-4-(2,5-dichloro-1-pyrrolyl)phenyl-N'-2,6-difluoro-
benzoylurea, m.p. 206-208°;
- 10 132. N-3,5-dichloro-4-(2,3,4,5-tetrachloro-1-pyrrolyl)phenyl-N'-2,6-difluoro-
benzoylurea, m.p. 244-245°;
133. N-3,5-dichloro-4-(3,4-dichloro-1-pyrrolyl)phenyl-N'-2,6-difluoro-
benzoylurea, m.p. 236-239°;
134. N-3,5-dichloro-4-[3-chloro-4-(2,4-dichlorophenyl)-1-pyrrolyl]phenyl-N'-
15 2,6-difluorobenzoylurea, m.p. 200-206°;
135. N-3,5-dichloro-4-(4,5,6,7-tetrahydroisoindol-2-yl)phenyl-N'-2-chloro-
benzoylurea, m.p. 230-231°;
136. N-3,5-dichloro-4-(2,5-dichloro-1-pyrrolyl)phenyl-N'-2-chlorobenzoylurea;
137. N-3,5-dichloro-4-(2,3,4,5-tetrachloro-1-pyrrolyl)phenyl-N'-2-chloro-
20 benzoylurea, m.p. 234-235°;
138. N-3,5-dichloro-4-(3,4-dichloro-1-pyrrolyl)phenyl-N'-2-chlorobenzoyl-
urea, m.p. 220-221°;
139. N-3,5-dichloro-4-[3-chloro-4-(2,4-dichlorophenyl)-1-pyrrolyl]phenyl-N'-
2-chlorobenzoylurea, m.p. 177-181°;
- 25 140. N-3,5-dichloro-4-(4,5,6,6-tetrahydroisoindol-2-yl)phenyl-N'-2-chloro-5-
fluorobenzoylurea;
141. N-3,5-dichloro-4-[3,4-bis(trifluoromethyl)-1-pyrazolyl]phenyl-N'-2-chloro-
5-fluorobenzoylurea;
142. N-3,5-dichloro-4-(4,5-dichloro-1-benzotriazolyl)phenyl-N'-2-chloro-5-
30 fluorobenzoylurea;
143. N-3,5-dichloro-4-(4,5,6,7-tetrahydroisoindol-2-yl)phenyl-N'-2-chloro-
benzoylthiourea;
144. N-3,5-dichloro-4-(3,4-dichloro-1-pyrrolyl)phenyl-N'-2-chlorobenzoyl-
thiourea;

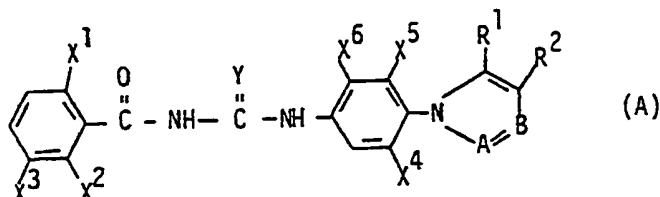
145. N-3,5-dichloro-4-[3,4-bis(trifluoromethyl)-1-pyrazolyl]phenyl-N'-2-chlorobenzoylthiourea;
146. N-3,5-dichloro-4-[4-chloro-3-(4-chlorophenyl)-1-pyrazolyl]phenyl-N'-2-chlorobenzoylthiourea;
- 5 147. N-3,5-dichloro-4-(4,5-dichloro-1-benzotriazolyl)phenyl-N'-2-chlorobenzoylthiourea;
148. N-3,5-dichloro-4-[4-chloro-3-(4-chlorophenyl)-1-pyrazolyl]phenyl-N'-2,6-difluorobenzoylurea, m.p. 166-167.5°.

10 BIOLOGICAL ACTIVITY

Example 4

Early (0-24 hr) third instar larvae of the tobacco budworm, Heliothis virescens, are topically treated on the dorsal abdomen with 1 microlitre of acetone dilution of the test compound at the concentration to be tested.

- 15 The treated larvae are placed on artificial diet in individual cells of a plastic grid contained in a covered plastic petri dish. The containers are held at 27°C, 16 hour photoperiod until all larvae are either dead or have molted to fifth instar larvae. In general, insecticidal activity is observed after application of from about 0.004 to 0.070 microgram test compound (4 to
- 20 70 ppm) per insect.

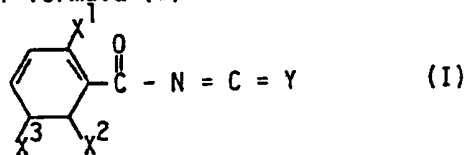
CLAIMS1. Compounds of formula (A)

- wherein, each of X^1 , X^2 , X^3 and X^5 is independently hydrogen, halogen or C_{1-4} alkyl;
- X^4 is hydrogen, halogen, unsubstituted or halogenated C_{1-4} alkyl or COOR;
- X^6 is hydrogen, halogen, C_{1-8} alkyl or COOR';
- Y is oxygen or sulfur;
- A is nitrogen or $C-R^4$;
- B is nitrogen or $C-R^3$;
- each of R^1 and R^4 is independently hydrogen, halogen, halogenated C_{1-8} alkyl, unsubstituted or halogenated C_{1-8} alkoxy, unsubstituted or halogenated C_{1-8} alkylthio or; aryl, aryloxy or arylthio unsubstituted or substituted with 1 to 4 halogen atoms or with a CF_3 , C_{1-4} alkyl or C_{1-4} alkoxy group and 0 to 3 halogen atoms;
- each of R^2 and R^3 is independently hydrogen; halogen; cyano; unsubstituted or halogenated C_{1-8} alkyl; unsubstituted or halogenated C_{1-8} alkoxy; unsubstituted or halogenated C_{1-8} alkylthio; COOR"; aryl, aryloxy or arylthio unsubstituted or substituted with 1 to 4 halogen atoms or with a C_{1-4} alkyl, C_{1-4} alkoxy or CF_3 group and 0 to 3 halogen atoms;
- or either R^1 and R^2 or R^2 or R^3 can together form a bridging group of 4 carbon atoms, saturated or unsaturated, and optionally substituted with 1 to 4 halogen atoms or with a trifluoromethyl group and 0 to 3 halogen atoms;
- each of R, R' and R" is hydrogen or C_{1-8} alkyl;
- with the proviso that where A is $C-R^4$ and B is $C-R^3$, not all of R^1 , R^2 , R^3 and R^4 may be hydrogen.

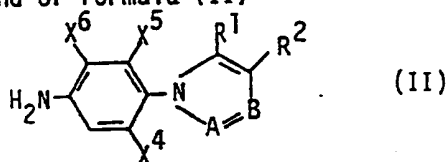
2. A compound according to Claim 1 wherein A is nitrogen and B is C-R³.
3. A compound according to Claims 1 or 2 wherein any aryl, aryloxy or arylthio is unsubstituted or mono- or disubstituted with one methyl, methoxy or CF₃ group and zero or one halogen or with one or two halogen, and whereby aryl
- 5 - as such or in the terms aryloxy and arylthio - refers to naphthyl, phenyl, pyridyl or thienyl.
4. A compound according to Claim 3, wherein Y is O.
5. A compound according to Claim 3 or 4, wherein each of X¹, X² and X³ is independently H or halogen,
- 10 X⁴ is H, halogen, CH₃ or CF₃,
 X⁵ is H, halogen or CH₃,
 X⁶ is H or halogen,
 each of R¹ and R² is independently H, halogen or CF₃,
 R³ is H, halogen, C₁₋₄ alkyl or CF₃ whereby one of R¹, R² and R³ may
- 15 also be halophenyl, dihalophenyl, methylphenyl or trifluoromethylphenyl and/or
 R¹ and R² together may form a bridging group of the formula CH=C-CH=CH, which group is unsubstituted or mono- or dihalogenated, or
 R² and R³ together form a bridging group of formula (CH₂)₄.
- 20 6. A compound according to Claim 5, wherein X¹ is halogen, X³ and X⁶ are H, X⁴ is halogen or CH₃ and R³ is H, halogen, CF₃ or halophenyl.
7. A compound according to Claim 6 selected from
- a) N-3,5-dichloro-4-[4-chloro-3-(4-chlorophenyl)-1-pyrazolyl]-phenyl-N'-2,6-difluorobenzoylurea,
- 25 b) N-3,5-dimethyl-4-[4-chloro-3-(4-chlorophenyl)-1-pyrazolyl]-phenyl-N'-2,6-difluorobenzoylurea,
- c) N-3,5-dichloro-4-(4-bromo-1-pyrazolyl)-phenyl-N'-2-chlorobenzoylurea,
- d) N-3,5-dichloro-4-(3,4-dibromo-1-pyrazolyl)phenyl-N'-2-
- 30 chlorobenzoylurea,

- e) N-3,5-dichloro-4-(4,5-dichloro-3-trifluoromethyl-1-pyrazolyl)phenyl-N'-2-chlorobenzoylurea,
 f) N-3,5-dichloro-4-[3-(4-chlorophenyl)-1-pyrazolyl]-
 5 phenyl-N'-2-chlorobenzoylurea,
 g) N-3,5-dichloro-4-(3,4,5-trichloro-1-pyrazolyl)phenyl-
N'-2-chlorobenzoylurea,
 h) N-3,5-dichloro-4-(4,5-dichloro-3-trifluoromethyl-1-pyrazolyl)phenyl-
N'-2-fluorobenzoylurea,
 10 i) N-3,5-dichloro-4-[3-(4-bromophenyl)-1-pyrazolyl]-
 phenyl-N'-2-fluorobenzoylurea.

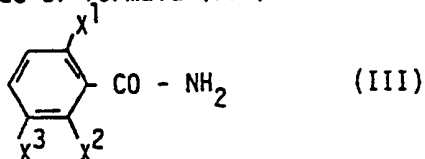
8. A pesticidal composition comprising a compound as defined in any one of Claims 1 to 7 and an agriculturally acceptable diluent.
 9. A method of combatting pests which comprises applying to the pest or its
 15 locus a pest-controlling amount of a compound of formula (A) as defined in any one of Claims 1 to 7.
 10. A process for preparing a compound of Claims 1 to 7 which comprises
 a) reacting a compound of formula (I)



wherein X^1 , X^2 , X^3 and Y are as defined in Claim 1,
 15 with a compound of formula (II)

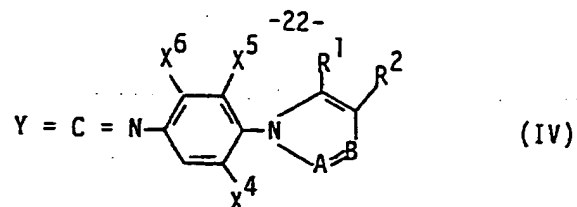


wherein X^4 , X^5 , X^6 , R^1 , R^2 , A and B are as defined in Claim 1,
 or by b) by reacting a benzamide of formula (III)



wherein X^1 , X^2 and X^3 are as defined in Claim 1,
 with a compound of formula (IV)

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wherein Y, R¹, R², X⁴, X⁵, X⁶, A and B are as defined in Claim 1.

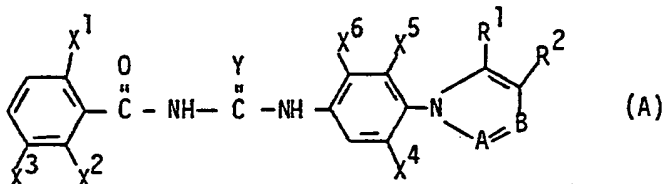
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CLAIMS

1. A pesticidal composition comprising a compound of formula (A)



wherein, each of X^1 , X^2 , X^3 and X^5 is independently hydrogen, halogen or

5 C_{1-4} alkyl;

X^4 is hydrogen, halogen, unsubstituted or halogenated C_{1-4} alkyl or $COOR$;

X^6 is hydrogen, halogen, C_{1-8} alkyl or $COOR'$;

Y is oxygen or sulfur;

A is nitrogen or $C-R^4$;

10 B is nitrogen or $C-R^3$;

each of R^1 and R^4 is independently hydrogen, halogen, halogenated C_{1-8} -alkyl, unsubstituted or halogenated C_{1-8} alkoxy, unsubstituted or halogenated C_{1-8} alkylthio or; aryl, aryloxy or arylthio unsubstituted or substituted with 1 to 4 halogen atoms or with a CF_3 ,

15 C_{1-4} alkyl or C_{1-4} alkoxy group and 0 to 3 halogen atoms;

each of R^2 and R^3 is independently hydrogen; halogen; cyano; unsubstituted or halogenated C_{1-8} alkyl; unsubstituted or halogenated C_{1-8} alkoxy; unsubstituted or halogenated C_{1-8} alkylthio; $COOR''$; aryl, aryloxy or arylthio unsubstituted or substituted with 1 to 4 halogenatoms or with a C_{1-4} alkyl, C_{1-4} alkoxy or CF_3 group and 0 to 3 halogen atoms; or either R^1 and R^2 or R^2 and R^3 can together form a bridging group of 4 carbon atoms, saturated or unsaturated, and optionally substituted with 1 to 4 halogen atoms or with a trifluoromethyl group and 0 to 3 halogen atoms;

25 each of R , R' and R'' is hydrogen or C_{1-8} alkyl;

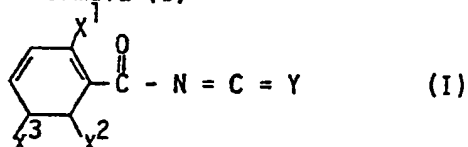
with the proviso that where A is $C-R^4$ and B is $C-R^3$, not all of R^1 ,

R^2 , R^3 and R^4 may be hydrogen, and an agriculturally acceptable diluent.

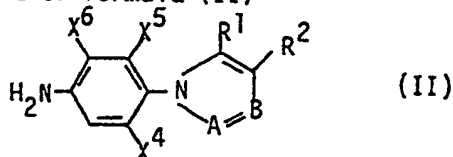
2. A composition according to Claim 1 wherein A is nitrogen and B is C-R³.
3. A composition according to Claims 1 or 2 wherein any aryl, aryloxy or arylthio is unsubstituted or mono- or disubstituted with one methyl, methoxy or CF₃ group and zero or one halogen or with one or two halogen, and whereby aryl - as such or in the terms aryloxy and arylthio - refers to naphthyl, phenyl, pyridyl or thienyl.
4. A composition according to Claim 3, wherein Y is O.
5. A composition according to Claim 3 or 4, wherein
- 10 each of X¹, X² and X³ is independently H or halogen,
X⁴ is H, halogen, CH₃ or CF₃,
X⁵ is H, halogen or CH₃,
X⁶ is H or halogen,
each of R¹ and R² is independently H, halogen or CF₃.
- 15 R³ is H, halogen, C₁₋₄ alkyl or CF₃ whereby one of R¹, R² and R³ may also be halophenyl, dihalophenyl, methylphenyl or trifluoromethylphenyl and/or
R¹ and R² together may form a bridging group of the formula CH=C-CH=CH, which group is unsubstituted or mono- or dihalogenated, or
- 20 R² and R³ together form a bridging group of formula (CH₂)₄.
6. A composition according to Claim 5, wherein X¹ is halogen.
7. A composition according to Claim 6,
wherein X³ and X⁶ are H,
X⁴ is halogen, CH₃ or CF₃,
25 X⁵ is halogen or CH₃
and R³ is H, halogen, CF₃ or halophenyl.

8. A process for preparing a compound of Claims 1 to 7 which comprises

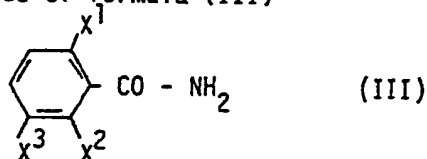
a) reacting a compound of formula (I)



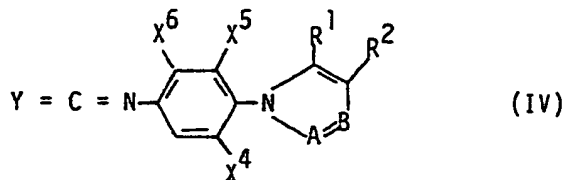
wherein X^1 , X^2 , X^3 and Y are as defined in Claim 1,
with a compound of formula (II)



5 wherein X^4 , X^5 , X^6 , R^1 , R^2 , A and B are as defined in Claim 1,
or by b) by reacting a benzamide of formula (III)



wherein X^1 , X^2 and X^3 are as defined in Claim 1,
with a compound of formula (IV)



wherein Y, R^1 , R^2 , X^4 , X^5 , X^6 , A and B are as defined in Claim 1.